

# The Photodegradation of Polypropylene. IV. UV Stabilizer Decomposition

D. J. CARLSSON, D. W. GRATAN, T. SUPRUNCHUK, and D. M. WILES, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A 0R9*

## Synopsis

The destruction of various UV stabilizers in polypropylene films during irradiation has been examined both in the presence and absence of air and oxidation products. Although some stabilizers were destroyed in the absence of oxygen, all were more sensitive when irradiated in the presence of air. Several stabilizers were highly effective but were destroyed so rapidly that photoprotection of the polymer must have resulted from stabilizer products. Work with preoxidized polymer and with model hydroperoxides and peroxides indicated that most stabilizers were destroyed by the attack of oxygen-centered radicals, with peroxy radical attack appearing to dominate.

## INTRODUCTION

Many classes of additives have now been developed for the prevention or reduction of the photo-oxidative degradation of polypropylene (PPH).<sup>1</sup> These additives seem to operate by several mechanisms, some of which can be ranked in order of increasing practical importance<sup>1</sup> as follows: excited chromophore deactivation < singlet oxygen ( $^1\text{O}_2$ ,  $^1\Delta_g$ ) quenching < UV absorption < hydroperoxide decomposition < radical scavenging. However the fact that an additive can operate by one (or more) of these mechanisms does not necessarily mean that the compound is an efficient photostabilizer. Other physical and chemical properties of the stabilizer must also be considered. For example, stabilizer mobility<sup>2</sup> and compatibility<sup>3</sup> play a role in determining stabilizer effectiveness. An equally important aspect is the resistance of the stabilizer to chemical decomposition either in the course of its photoprotective role or by side reactions in the degrading polymer. Processes which can be expected to destroy the stabilizer include its direct photolysis or photo-oxidation and also attack by reactive species which result during the photo-oxidation of the polymer ( $^1\text{O}_2$ ,  $-\text{OOH}$  groups,  $\text{R}\cdot$ ,  $\text{RO}_2\cdot$ ,  $\text{RO}\cdot$ ,  $\cdot\text{OH}$ , etc.).<sup>4</sup> A knowledge of these destructive side reactions might allow the development of more resistant modifications of a given stabilizer type or indicate the way in which a second additive might be used to protect the main UV stabilizer. The effect of  $^1\text{O}_2$  exposure on some stabilizers (especially phenol derivatives) has already been discussed.<sup>2</sup>

In this paper we discuss the various chemical processes which cause the decomposition of UV stabilizers, both in PPH and in model liquid systems. This discussion is confined to broad generalities; specific details of reactions involving separate UV stabilizer classes will be given in future publications.

## EXPERIMENTAL

Both commercial isotactic polypropylene (PPH) film (Enjay, 25  $\mu\text{m}$ ) and laboratory-prepared films ( $\sim 40$   $\mu\text{m}$  from Montecatini PPH power) were used. Stabilizer additives were compounded into films by first dissolving them in a volatile solvent ( $\text{CH}_2\text{Cl}_2$ , xylene or isooctane) and then evaporating this solution onto  $\sim 1$  g PPH. This dried power was pressed into films between  $5 \times 5$   $\text{cm}^2$  quartz plates under a  $\text{N}_2$  atmosphere at  $225^\circ\text{C}$  and then immediately quenched in dry ice-methanol. Stabilizer dispersion on PPH power by the use of xylene gave unreliable results. Treatment of PPH with only this solvent gave film UV lifetimes appreciably shorter than films from fresh PPH power, presumably because of xylene residues. Methylene chloride and isooctane treatment of the PPH powder had no effect on film photostability. Stabilizers were introduced into preformed commercial film by immersion of the film in isooctane solutions of the stabilizers for 50–200 hr. The films were then briefly rinsed in isooctane and vacuum dried.

Stabilizer concentrations in films were estimated from ultraviolet (UV) spectroscopy on a Cary 15 spectrophotometer, using solution standards. The buildup of photo-oxidation products was measured by infrared (IR) spectroscopy with Beckman IR 8 and 4210 spectrometers. The electron spin resonance (ESR) spectra of N-oxyl radicals were measured on a Varian E-4 spectrometer. The  $g$  values of the broad  $>\text{NO}\cdot$  signals were 2.0059 gauss,  $\sim 2$  G width in the liquid phase, but  $\sim 8$  G in PPH films.

Tetramethylpiperidines and their products were measured by liquid chromatography (LC), using a Waters ALC 201 fitted with UV and refractive index detectors and a Waters  $\mu$ -Bondapak CN column. Isocratic separations employed an isopropanol/hexane mixture (3:97 v-%). The piperidines were extracted from  $\sim 0.1$ -g film samples with methylene chloride. Fractions were characterized by retention times, using known compounds, and by IR and NMR. Tetramethylpiperidines in liquid photolyses were also monitored by gas chromatography, using an OV-101 column with temperature programming from  $75^\circ$  to  $140^\circ\text{C}$ .

Photo-oxidations and irradiations were carried out either with a 6000-W xenon arc Weather-Ometer (Atlas) or with the collimated beam from an Osram superpressure mercury arc (500 W) filtered through a Corning CS 1-64 filter ( $\lambda > 310$  nm).

Stabilizer solutions were irradiated in 0.1-cm quartz cells fitted with quartz-Pyrex graded seals. *tert*-Octyl hydroperoxide (Lucidol Corp.) was purified by formation of the sodium salt and regeneration of the hydroperoxide by  $\text{CO}_2$ .<sup>5</sup> Iodometry indicated  $>98\%$  purity of the hydroperoxide.

## RESULTS

The UV-visible absorption spectra of stabilizers studied here are shown in Figures 1–3. Stabilizer nomenclature and abbreviations are listed in Table I.

### Stabilizer Loss During Irradiation in PPH

To examine photolytic resistance and resistance to the photo-oxidative environment in PPH, 40- $\mu\text{m}$  films of stabilizers in PPH were prepared. Stabilizer

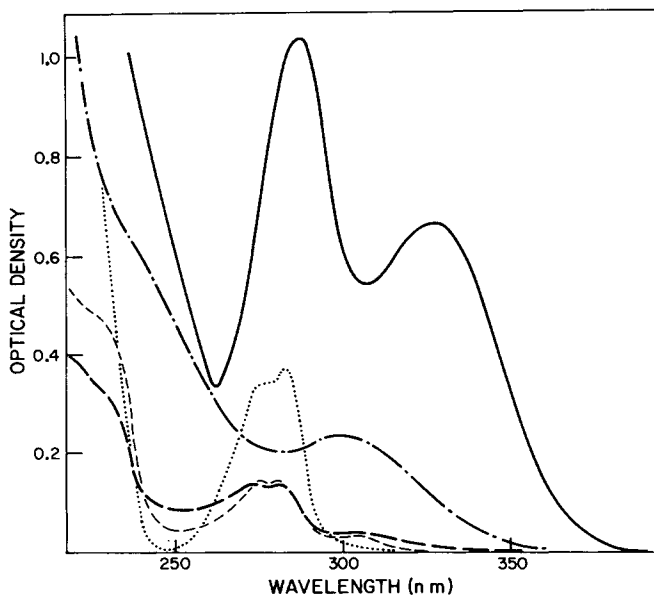


Fig. 1. UV absorption spectra of stabilizers in PPH film; 40- $\mu$ m films, stabilizers at 0.5 wt-%: (.....) P-1; (---) P-2; (—) P-3; (-·-) Ni-1; (- - -) Ni-3.

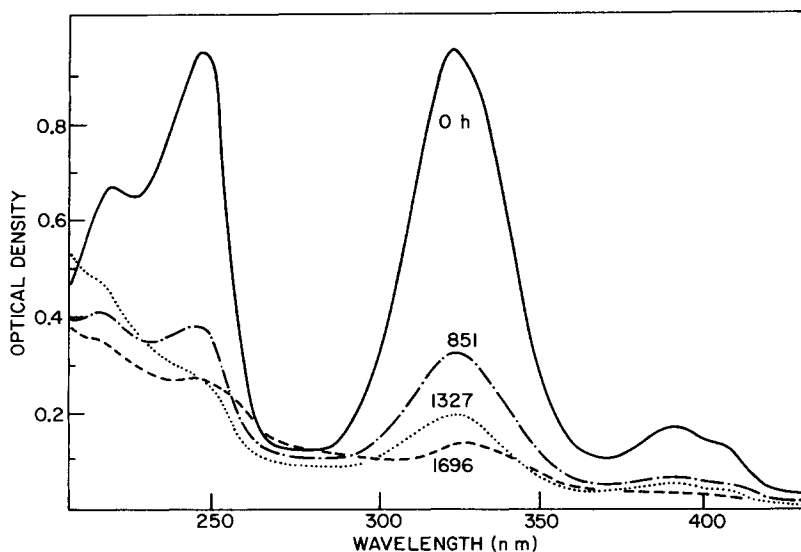


Fig. 2. UV changes on irradiating Ni-2 in PPH film in air; 40- $\mu$ m film, Ni-2 at 0.1 wt-%. Times refer to Xe arc Weather-Ometer periods.

concentrations in the 0.1–0.5 wt-% range were selected so as to be within the detection range of the analytical technique chosen to follow their consumption. In addition, this range is consistent with the levels commonly found in commercial PPH films and fibers. Two film samples containing each stabilizer were then exposed in the Xe arc Weather-Ometer, one film being directly irradiated in air, the second film being irradiated inside a sealed  $N_2$ -filled 1-cm-path quartz cell. The UV spectra of both samples were periodically monitored to follow changes in stabilizer concentration and composition. The IR spectra of the

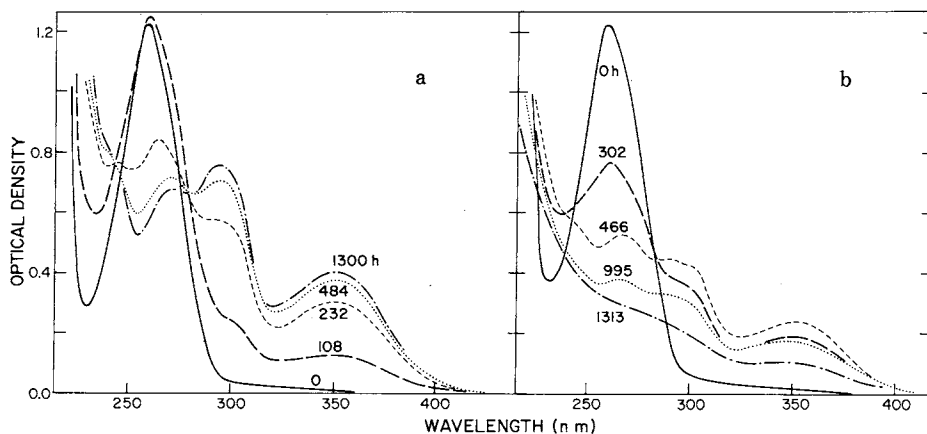


Fig. 3. UV changes on irradiating P-4 in PPH film; 40- $\mu$ m film, P-4 at 0.4 wt-%: (a) under  $N_2$ ; (b) in air. Times refer to Xe arc Weather-Ometer periods.

air-irradiated samples were also monitored frequently to follow the photo-oxidation of the polymer. Photo-oxidation usually accelerated rapidly at the end of the induction period. Brittle failure on flexing of a film usually occurred when  $OD_{3400}$  reached  $\sim 0.03$ .

For TMP-1 and TMP-2, UV spectral changes were obscured by the PPH UV scattering at short wavelengths. A clearer indication of stabilizer changes was given by ESR spectroscopy and by the gas- or liquid-chromatographic analysis of film extracts.

For most of the stabilizers studied, UV spectroscopy indicated a monotonous reduction in stabilizer absorption during air or  $N_2$  irradiation, Figure 2. Only P-4 shows the formation of new absorptions under  $N_2$ , Figure 3(a), and to a lesser extent under air, Figure 3(b). ESR showed the formation of a low concentration of stable N-oxyl radicals from TMP-1, Figure 4(b).

The kinetic loss of each stabilizer under  $N_2$  and air and the buildup of PPH photo-oxidation products are shown in Figures 4, 5, and 6. The buildup of carbonyl ( $>C=O$ , at  $\sim 1715\text{ cm}^{-1}$ ) and hydroxyl groups (hydroperoxide + alcohol at  $\sim 3400\text{ cm}^{-1}$ ) in unstabilized PPH is shown in Figure 6(a) for comparison purposes. The times for each additive to degrade to half its initial value in PPH, both under irradiation in  $N_2$  ( $\tau_{N_2}$ ) and in air ( $\tau_{O_2}$ ), are listed in Table I and are derived from the curves shown in Figures 4–6.

### Stabilizer Loss During Irradiation in PPOOH

To investigate the effect of the photolysis products from PPOOH on UV stabilizers, PPH films (25  $\mu$ m) were preoxidized by  $\sim 60$  hr of irradiation in the Weather-Ometer to give a PPOOH concentration of  $\sim 5 \times 10^{-2}M$  by iodometry and stabilizers subsequently introduced by solution immersion. These PPOOH + stabilizer films were exposed in the Weather-Ometer or to the filtered mercury arc ( $\lambda > 310\text{ nm}$ ) either in air or under  $N_2$ . Only some stabilizers which did not decompose PPOOH thermally were examined. Ni-2 and TMP-1 decompose PPOOH quite rapidly and could not be studied.

Ni-1 showed a steady loss on exposure under  $N_2$  (60% loss in  $\sim 90$  hr), as did P-4. However, P-4 did not produce any of the new absorptions observed pre-

TABLE I  
Effects of Irradiation of UV Stabilizers

Stabilizer	Photoresistance in PPH			Photoresistance in isooctane		
	Concn., wt-%	Under N <sub>2</sub> τ <sub>N<sub>2</sub></sub> , hr	Under air τ <sub>O<sub>2</sub></sub> , hr	Concn., wt-%	τ <sub>0</sub> , hr	τ <sub>0</sub> /τ <sub>ox</sub> ( <i>t</i> -BuOO- <i>t</i> -Bu) <sup>b</sup>
P-1 2,6-Di- <i>t</i> -butyl-4-methylphenol	0.5	110	17	0.072	19	1.4
P-2 Octadecyl 3-(3',5'-di- <i>t</i> -butyl-4'-hydroxyphenyl)-propionate	0.5	450	200	0.082	21	1.2
P-3 2-Hydroxy-4-dodecyloxybenzophenone	0.5	>6000	1300	0.030	40	0.95
P-4 2,4-Di- <i>t</i> -butylphenyl (4'-hydroxy-3'5'-di- <i>t</i> -butylbenzoate)	0.5	>5000 <sup>c</sup>	1100 <sup>c</sup>	0.040	9	1.3
TMP-1 2,2,6,6-Tetramethyl-4-hydroxypiperidine	0.1	>120	50	0.063	>100	(τ <sub>ox</sub> = 32 h)
TMP-2 2,2,6,6-Tetramethyl-4-hydroxypiperidine-N-oxyl	0.1	~300	50	0.067	33	1.1
Ni-1 Ni(II) 2,2'-Thiobis(4- <i>t</i> -octylphenolate)- <i>n</i> -butylamine	0.5	>>2000	700	0.040	60	2.8
Ni-2 Ni(II) Di- <i>n</i> -butyl dithiocarbamate	0.1	~6000	500	0.018	120	N.D. <sup>d</sup>
Ni-3 Ni(II) Di(O- <i>n</i> -butyl 3,5-di- <i>t</i> -butyl-4-hydroxybenzylphosphonate)	0.5	~2000	400	0.046	22	3.1

<sup>a</sup> *t*-Octyl hydroperoxide concentration  $2.0 \times 10^{-3}M$ .

<sup>b</sup> Di-*t*-butyl peroxide concentration  $1.2 \times 10^{-3}M$ .

<sup>c</sup> Stability of the photo-Fries product.

<sup>d</sup> Not determined because TMP-1 and Ni-2 are hydroperoxide decomposers.

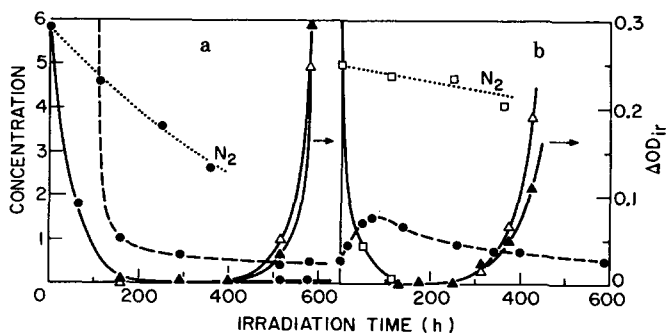


Fig. 4. Changes on irradiating TMP-1 and -2 in PPH film; 40 $\mu$ m film. Data for films irradiated by Xe arc Weather-Ometer, in air except for those labeled N<sub>2</sub>: (a) TMP-2 concentrations  $M \times 10^3$  (—●—) and  $M \times 10^4$  (—●—). (b) TMP-1 concentrations  $M \times 10^3$  (□); TMP-2 product concentrations  $M \times 10^4$  (—●—). PPH oxidation products (from IR): (▲) —OH; (Δ) >C=O.

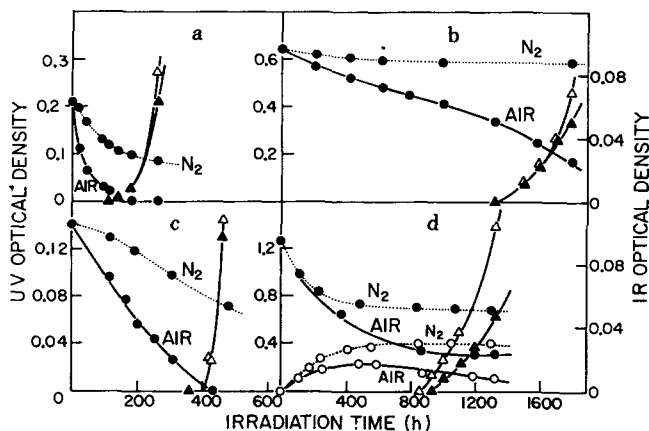


Fig. 5. Changes on irradiating phenols in PPH film; 40- $\mu$ m film. Irradiation conditions as in Figure 4. Irradiation in air (—) or N<sub>2</sub> (···). PPH oxidation products (from IR): (Δ) >C=O; (▲) —OH. Stabilizers (at 0.5 wt-%): (a) P-1, OD at 280 nm; (b) P-3, OD at 326 nm; (c) P-2, OD at 280 nm; (d) P-4, OD's at 260 nm (●) and 350 nm (○).

viously (Fig. 3). P-3 showed little change (only ~6% loss in 90 hr under N<sub>2</sub>). Under air irradiation in the Weather-Ometer, PPOOH film containing the hindered phenols P-1 and -2 showed a distinctly different behavior. P-1 was destroyed extremely rapidly (<100 hr) Figure 7(a), and photo-oxidation then occurred. P-2 was similarly destroyed, Figure 7(b), but photo-oxidation was delayed a further 200 hr after the complete loss of P-2. Ni-3 (~0.7 wt-%) was also rapidly destroyed in ~100 hr, but photo-oxidation was suppressed until ~250 hr. Ni-1 (0.5 wt-%) was destroyed steadily over ~250 hr when photo-oxidation accelerated. TMP-2 (0.08 wt-%) in the presence of —OOH groups behaved virtually identically to that shown in Figure 4(a); if anything, photo-oxidation was suppressed somewhat longer than in the PPH film.

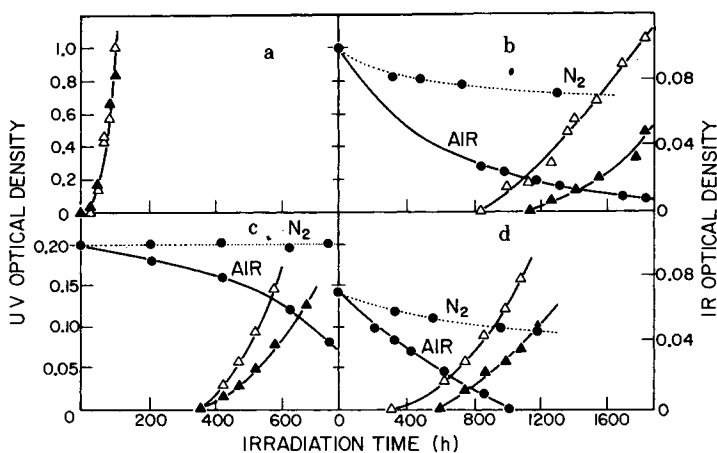


Fig. 6. Changes on irradiating Ni-chelates in PPH films; 40- $\mu$ m films. Irradiation conditions and atmospheres as in Figure 5. PPH oxidation products (from IR): ( $\blacktriangle$ ) —OH; ( $\triangle$ ) >C=O. Stabilizers: (a) none; (b) Ni-2 at 0.13%, OD at 324 nm; (c) Ni-1 at 0.5 wt-%, OD at 305 nm; and (d) Ni-3 at 0.5 wt-%, OD at 280 nm.

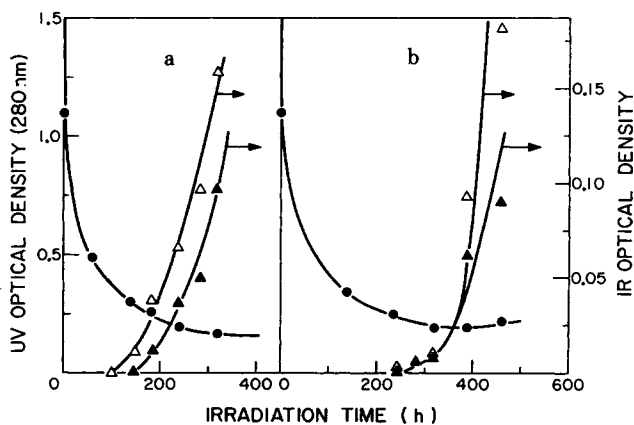


Fig. 7. Irradiation of phenols in PPOOH film; 24- $\mu$ m film, preoxidized to  $6 \times 10^{-2}M$  in hydroperoxide. Irradiations in air with the Xe arc Weather-Ometer. PPH oxidation products (from IR): ( $\blacktriangle$ ) —OH; ( $\triangle$ ) >C=O. Stabilizers: (a) P-1 at 2.5 wt-%; and (b) P-2 at 4.0 wt-%.

### Stabilizer Reactions with Free Radicals

Several of the UV stabilizers listed in Table I were dissolved in isoctane and exposed to UV irradiation from the filtered Hg arc ( $\lambda > 310$  nm) under  $N_2$ . In some cases either di-*tert*-butyl peroxide or *tert*-octyl hydroperoxide was present in the solution. All of the stabilizers were destroyed under these conditions, as shown by UV spectroscopy, although the rates of destruction varied greatly. The effects of irradiation on solutions of P-3 are shown in Figure 8. P-3 destruction was not accelerated by the presence of either the peroxide or the hydroperoxide. Because all other stabilizers decayed monotonously to zero, their rates of loss are most conveniently compared as  $\tau_0/\tau_{ox}$  ratios, where  $\tau_0$  represents the time for the stabilizer to photolyze to half its initial level in isoctane under  $N_2$  and  $\tau_{ox}$  refers to the half-life in the presence of the peroxide or hydroperoxide. These values are collected in Table I. Even P-4 decayed monotonously to zero when irradiated in isoctane, without formation of the new peaks seen when irradiated in the polymer (Fig. 3).

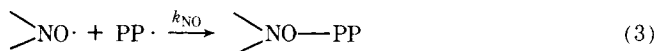




vealed no stabilizer residues on the cell walls. Thus, volatilization out of the films during irradiation appeared negligible. However, irradiation with constant air flow over the surface could well contribute to some physical loss.

For all of the stabilizers studied, irradiation in air caused marked losses ( $\tau_{O_2} \ll \tau_{N_2}$ , Table I). In most cases the additive was found to have decreased by a factor of  $\sim 10$  at the onset of photo-oxidation (P-1, -2, and -4, TMP-1 and -2, Ni-2 and -3, Figs. 4-6). In several cases a comparison of oxidation product formation (from IR) and changes in the UV spectra indicated that it is most likely a product of the additive which is the effective stabilizer for a considerable fraction of the sample lifetime [TMP-1 and -2 and P-4, Figs. 4 and 5(d)], the initial additive being quickly destroyed.

Both TMP-1 and TMP-2 are destroyed rapidly during PPH irradiation in air (Fig. 4). However, PPH photoprotection persists at the low residual  $>NO\cdot$  concentrations ( $\sim 1 \times 10^{-4}M$ , from an initial stabilizer level of  $\sim 5 \times 10^{-3}M$ ). Similar data have been published by Shylapintokh et al.<sup>7</sup> Nitroxides are suggested to photostabilize by intercepting alkyl radicals<sup>8</sup>:



This interception prevents propagation of the alkyl radicals to generate (photo unstable) hydroperoxide in the chain reaction (1) and so stabilizes the polymer. Although reaction (3) is fast for alkyl radicals ( $k_{NO} \sim 5 \times 10^8 M^{-1} \text{sec}^{-1}$ ),<sup>9</sup>  $k_{O_2}/k_{NO}$  is reported to be  $\sim 10$  for the styryl radical.<sup>10</sup> Then for the residual  $>NO\cdot$  level of  $\sim 1 \times 10^{-4}M$  and an  $O_2$  concentration of  $\sim 1 \times 10^{-3}M$  for 50% crystalline PPH in contact with air,<sup>11</sup>

$$\frac{k_{O_2}[PP\cdot][O_2]}{k_{NO}[PP\cdot][NO\cdot]} \approx 100$$

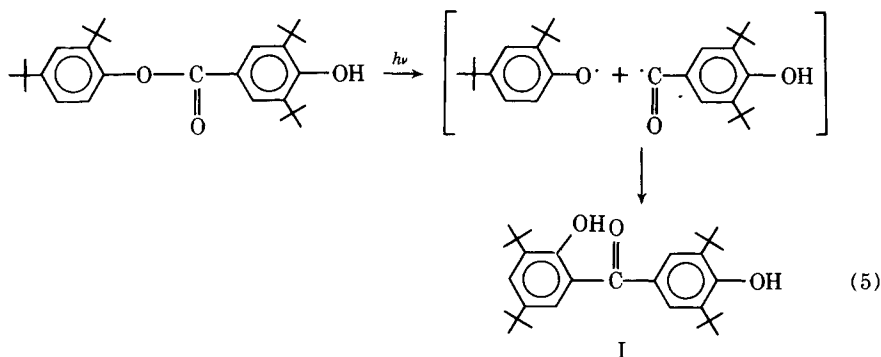
This implies that the residual  $>NO\cdot$  level cannot be the sole source of photoprotection for the bulk of the lifetime of PPH films stabilized by TMP-1 and TMP-2, unless selective association occurs. That is, the  $>NO\cdot$  species may diffuse to polar sites such as the residual  $-OOH$  groups. The local concentration of  $>NO\cdot$  might allow interception of radicals from reaction (2), even at the  $1 \times 10^{-4}M$  average level if association (for example, by hydrogen bonding) is sufficiently strong. This complexing has been recently observed between *tert*-butyl hydroperoxide and TMP-2 in isoctane.<sup>12</sup>

An alternative explanation involves the  $>N-O-PP$  species from reaction (3). The rapid conversion of TMP-1 and TMP-2 to  $>N-O-PP$  by reaction with macroalkyl radicals means that the stabilizer becomes grafted to the polymer backbone and completely immobile.<sup>13</sup> This will make the stabilizer residues completely resistant to volatilization and leaching. Shilov and Denisov<sup>13</sup> have suggested that the  $>N-O-PP$  species can further react by scavenging  $PPO_2\cdot$ :



Indirect evidence for this process has been reported by Sudnik et al.<sup>8</sup> who found  $k_3 \sim 3 \times 10^2 M^{-1} \text{sec}^{-1}$  at 100°C. This process might just compete successfully with the slow  $\text{PPO}_2\cdot$  propagation, reaction (1b) ( $k_p \approx 0.05 M^{-1} \text{sec}^{-1}$  at 30°C).<sup>10</sup>

P-4 is known to undergo a photo-Fries rearrangement to give a 2-hydroxybenzophenone product,<sup>14,15</sup> reaction (5):



This species absorbs strongly at 355 nm, and its formation is clearly seen in Figure 3(a) for irradiation under  $\text{N}_2$ . From the published extinction coefficient for 2,4-dihydroxybenzophenone ( $\sim 1 \times 10^4$  at 340 nm),<sup>16</sup> the UV changes shown in Figure 3(a) indicate quantitative conversion to the photo-Fries product. This product is completely formed in  $\sim 500$  hr and is extremely photostable under  $\text{N}_2$ , Fig. 5(d). From Figures 3(b) and 5(c) it is apparent that much less photo-Fries product results from irradiation in air and that the photo-Fries product is itself slowly destroyed. The photo-Fries rearrangement usually involves scission to give a radical pair, as shown in reaction (5). In the presence of  $\text{O}_2$ , oxygen interception of the species is well known,<sup>17</sup> with a corresponding reduction in photo-Fries yield. In solution the radicals may diffuse apart before recombination, and in fact we observed no Fries product after irradiating P-4 in isoctane under  $\text{N}_2$ . Heller and Blattmann<sup>15</sup> also found little rearrangement product in solution photolyses.

Heller and Blattmann<sup>15</sup> have reported that the photo-Fries product I, reaction (5), is a poor stabilizer for PPH photo-oxidation, yet P-4 is an excellent UV stabilizer. This implies that it is neither P-4 nor I which is the active stabilizer but some other intermediate.

Irradiation of PPH in air in the absence of a stabilizer results in a roughly identical increase in the IR optical densities of  $-\text{OH}$  (at  $3400 \text{ cm}^{-1}$ ) and  $>\text{C}=\text{O}$  (at  $\sim 1715 \text{ cm}^{-1}$ ), as shown in Figure 6(a). In the presence of some stabilizers (P-1, P-2, P-3, TMP-1, TMP-2) this same relationship holds (Figs. 4 and 5). However with stabilizers P-4, Ni-1, Ni-2, and Ni-3,  $OD_{\text{OH}}$  lags appreciably behind  $OD_{>\text{C}=\text{O}}$ , Figures 5(d) and (6). This reduction in  $-\text{OH}$  products must reflect on the stabilization mechanism operating in each case. For example, it is consistent with hydroperoxide decomposition by the stabilizer, or by an intermediate, as has been reported for various Ni chelates.<sup>18-20</sup>

Irradiation under  $\text{N}_2$  of PPH films which were prephoto-oxidized to give PPOOH before the incorporation of a stabilizer showed that Ni-1 and P-4 were very rapidly destroyed, whereas P-3 was little affected. For example, no

photo-Fries products were detected from P-4 under these conditions. This is consistent with the destruction of the stabilizers by the macroalkoxy and  $\cdot\text{OH}$  radicals generated in the facile photocleavage of the PPOOH groups or  $\text{PPO}_2\cdot$  radicals generated by secondary reactions with PPOOH. Association between a stabilizer and the  $-\text{OOH}$  groups by, for example, hydrogen bonding could place the stabilizer in an ideal location to intercept (and be itself destroyed by) the PPOOH photocleavage products. UV spectral shifts and changes in the ESR splitting constants for TMP-2 in the presence of hydroperoxides do indicate strong association between stabilizer and hydroperoxide.<sup>12</sup> Irradiation in air of preoxidized PPH films containing stabilizers P-1, P-2, Ni-1, and Ni-3 showed rates of destruction appreciably higher than observed in PPH. Only TMP-2 protected equally effectively in both PPH and preoxidized PPH.

A comparison of stabilizer persistence in  $\text{O}_2$ -free isooctane solution during irradiation alone, in the presence of di-*tert*-butyl peroxide or in the presence of *tert*-octyl hydroperoxide, was used to differentiate stabilizer reactivity toward alkoxy radicals (from the peroxide photocleavage)<sup>2</sup> and alkoxy, hydroxyl, and peroxy radicals (from the hydroperoxide reactions).<sup>4,10</sup> These results are illustrated by Figure 8, and data are collected in Table I. Values of  $\tau_0/\tau_{ox}$  close to 1.0 imply that direct stabilizer photolysis is the major route for stabilizer destruction and that oxygen-centered radicals play a negligible role (e.g., P-3). Surprisingly, TMP-2 is not rapidly destroyed by the dominant radicals from hydroperoxide photolysis (presumably  $\text{RO}_2\cdot$ ).

In general, radicals derived from the hydroperoxide ( $\text{RO}\cdot$ ,  $\cdot\text{OH}$ ,  $\text{RO}_2\cdot$ ) were very much more effective in destroying stabilizers than the alkoxy radicals from the direct photocleavage of the peroxide (Table I). Only Ni-2 was rapidly destroyed by alkoxy radicals. This implies that  $\cdot\text{OH}$ , or more likely the longer-lived peroxy radicals produced after the hydroperoxide photolysis, are most effective in destroying stabilizers. This is consistent with the suggested importance of radical scavenging in photostabilization.<sup>1,19</sup>

Vink<sup>22</sup> has followed the  $\text{O}_2$  consumption of PPH films containing a few stabilizers over a range of concentrations and monitored stabilizer destruction. He also found extensive destruction of a P-3-like additive and Ni-1 during the induction period.

## CONCLUSIONS

(a) All effective UV stabilizers are progressively destroyed during the lifetime of photo-oxidizing PPH films.

(b) Several UV stabilizers are almost completely destroyed well before the end of the photo-oxidative lifetime of the PPH film. In these cases photoprotection must stem, at least in part, from stabilizer products.

(c) Most UV stabilizers are photostable in PPH in the absence of  $\text{O}_2$  but are destroyed by oxidative processes.

(d) Liquid-phase work with model systems indicates that many stabilizers are destroyed by oxygen-centered radical attack, probably mainly by peroxy radicals.

## References

1. D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C14**, 155 (1976).
2. O. Cicchetti, M. Dubini, P. Parrini, G. P. Vicario, and E. Buca, *Eur. Polym. J.*, **4**, 419 (1968).
3. G. Lappin, in *Encyclopedia of Polymer Science and Technology*, Vol. 14, Wiley, New York, 1971, p. 125.
4. D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C14**, 65 (1976).
5. D. J. Carlsson and D. M. Wiles, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2217 (1974).
6. D. J. Carlsson, A. Garton, and D. M. Wiles, *Macromolecules*, **9**, 695 (1976).
7. V. Y. Shlyapintokh, V. B. Ivanov, O. M. Khvostach, A. B. Shapiro, and E. G. Rozantsev, *Dokl. Acad. Nauk SSSR*, **225**, 1132 (1975).
8. M. V. Sudnik, M. F. Romantsev, A. B. Shapiro, and E. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2813 (1975).
9. S. Nigam, K. D. Asmus and R. L. Willson, *J. Chem. Soc. Farad. Trans. II*, 2324 (1976).
10. J. A. Howard, *Adv. Free Rad. Chem.*, **4**, 49 (1972).
11. S. G. Kiryusllim, O. E. Yakimchenko, Y. A. Shlyapnikov, G. G. Pariiskii, D. Y. Toptygin, and Y. S. Lebedev, *Vysokomol. Soedin.*, **17B**, 385 (1975).
12. D. W. Grattan, D. J. Carlsson, A. H. Reddoch, and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.*, in press.
13. Y. B. Shilov and E. T. Denisov, *Vysokomol. Soedin.*, **A16**, 2313 (1974).
14. G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).
15. H. J. Heller and H. R. Blattmann, *Pure Appl. Chem*, **30**, 145 (1972).
16. G. M. Ganz and W. G. Sumner, *Text. Res. J.*, **27**, 244 (1957).
17. D. J. Carlsson, L. H. Gan, R. D. Parnell, and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 683 (1973).
18. R. P. R. Ranaweera and G. Scott, *Eur. Polym. J.*, **12**, 825 (1976).
19. R. P. R. Ranaweera and G. Scott, *Eur. Polym. J.*, **12**, 591 (1976).
20. J. A. Howard and J. H. B. Chenier, *Can. J. Chem.*, **54**, 390 (1976).
21. E. Lissi, *Can. J. Chem.*, **52**, 2491 (1974).
22. P. Vink, *J. Polym. Sci.*, **C40**, 169 (1973).

Received April 28, 1977

Revised May 12, 1977